# Kinetic Study on the Adsorption of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane on Ag Nanoparticles in Chloroform: Implications for the Charge Transfer Complex of Ag-F<sub>4</sub>TCNQ

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**Keywords**: Ag nanoparticles; F<sub>4</sub>TCNQ; phase transfer; kinetics; electron transfer; surface interaction

## Abstract

In this study, the kinetics of the adsorption of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F<sub>4</sub>TCNQ) on the surface of Ag nanoparticles (Ag NPs) in chloroform have been intensively investigated, as the molecular doping is known to play a crucial role in

organic electronic devices. Based on the results obtained from UV-vis-NIR absorption spectroscopy, cryogenic transmission electron microscopy (cryo-TEM), scanning nano-beam electron diffraction (NBED) and electron energy loss spectroscopy (EELS), a two-step interaction kinetics has been proposed for the Ag NPs and F4TCNQ molecules, which includes the first step of electron transfer from Ag NPs to F4TCNQ indicated by the ionization of F4TCNQ, and the second step of the formation of Ag-F4TCNQ complex. The whole process has been followed via UV-vis-NIR absorption spectroscopy which reveals distinct kinetics at two stages: the instantaneous ionization and the long-term complex formation. The kinetics and the influence of the molar ratio of Ag NPs/F4TCNQ molecules on the interaction between Ag NPs and F4TCNQ molecules in the organic solution are reported herein for the first time. Furthermore, the control experiment with silica-coated Ag NPs manifests that the charge transfer at the surface between Ag NPs and F4TCNQ molecules is prohibited by a silica layer of 18 nm.

### Introduction

The energetics at organic/metal interfaces have attracted considerable research interest in recent years.<sup>1-5</sup> Electron donating/accepting molecules on metal surfaces have been used for tuning interfacial electronic structures, which facilitate improvements in the performance of organic optoelectronic devices such as light-emitting diodes, organic field-effect transistors and organic photovoltaics.<sup>6-8</sup> Among these molecules, 7,7,8,8-tetracyanoquinodimethane (TCNQ) is well known as a widely employed electron acceptor that enables the transfer of electrons from metals to organic molecules and leads to the formation of metal-TCNQ complex.<sup>9,10</sup> To explore the charge transfer and the complex formation, many methods have been applied such as electrochemical approach,<sup>11</sup> chemical vapor deposition,<sup>12</sup> and the photo-induced synthesis.<sup>13</sup> Although various

metal-TCNQ crystal structures, such as nanowires, clusters and so on have been reported,<sup>14, 15</sup> the formation of metal-TCNQ nuclei in these published methods is stochastic. Much less work has been conducted on the interaction mechanism between metal and TCNQ molecules. Xiao *et al* has revealed the whole formation procedure of the Ag-TCNQ nanowires in aqueous solutions containing Ag nanoparticles and TCNQ micro-particles, but only at macroscopic level.<sup>14</sup> Kinetic study on direct interactions between electron donating/accepting molecules and noble metals in solution is still a challenge.

Currently, growing interests have arisen in the fully fluorinated version of TCNQ, namely 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ).<sup>16-19</sup> This is linked not only to its similarity of the ability to exist in multiple as well as stable oxidation state with TCNQ, but also to its higher electron affinity of 4.93 eV (measured by the electrochemical method for single molecule in the solution of CH<sub>2</sub>Cl<sub>2</sub>),<sup>20, 21</sup> compared to 3.4 eV of TCNQ.<sup>22, 23</sup> Due to the high electron affinity, the neutral fluorinated quinonoid form can undergo a one electron reduction to form radical mono-anion F<sub>4</sub>TCNQ<sup>-</sup>, a further uptake of one electron transforms F<sub>4</sub>TCNQ<sup>-</sup> to  $F_4TCNQ^2$  afterwards. The conformational freedom of  $F_4TCNQ^2$  and  $F_4TCNQ^2$  is much larger than that of neutral F<sub>4</sub>TCNQ. It therefore allows F<sub>4</sub>TCNQ to be used as a strong electron acceptor for energy-level tuning of metal nanomaterial surfaces and inducing interface dipole, which endows metal nanoparticles like silver with a partially positive-charged surface. Such effect renders the composite system consisting of silver nanoparticles (electron donor) and F4TCNQ (electron acceptor) for the formation of Ag-F<sub>4</sub>TCNQ solid.<sup>24-26</sup> This has been first achieved by the spontaneous redox reaction, which forms Ag-F<sub>4</sub>TCNQ film on an Ag substrate.<sup>27</sup> Electrocrystallization approach is late developed by Le et al to obtain Ag-F4TCNQ solid in acetonitrile solution.<sup>28</sup> Wang et al have adopted a facile method in solution, in which Ag NPs with size of 610 nm and  $F_4TCNQ$  acetonitrile microemulsions are employed, to explore the synthesis of Ag NPs decorated Ag-F<sub>4</sub>TCNQ in the presence of F<sub>4</sub>TCNQ molecules and Ag NPs in microemulsion. However, due to the presence of a tiny amount of water that could induce the ionization of F<sub>4</sub>TCNQ, it fails to reveal the direct charge transfer and ionization between Ag NPs and F<sub>4</sub>TCNQ.<sup>29</sup> Chae *et al* used F<sub>4</sub>TCNQ molecules to increase the carrier activity of Ag NPs in silver-olefin complexation by preparing the PVP/AgNPs/F<sub>4</sub>TCNQ nanocomposites in ethanol. However, it is still ambiguous to reveal the interaction between F<sub>4</sub>TCNQ and Ag NPs in this system, as the F<sub>4</sub>TCNQ molecules were pre-ionized in ethanol.<sup>30</sup> In order to gain further insight into the direct relationship between Ag NPs and F<sub>4</sub>TCNQ molecules, it is of significance to integrate the systems in the organic liquid phase synchronously by avoiding water as the reactant.

Considering the localized surface plasmon resonance (LSPR) of Ag NPs and the absorption spectra of  $F_4TCNQ$  molecules can be directly tracked by UV-vis-NIR absorption spectroscopy, it is possible to follow the interaction of Ag NPs and  $F_4TCNQ$  molecules kinetically via UV-vis-NIR spectroscopy in the same solvent environment. Combining the merits of the phase-transfer modified Ag NPs and the organic molecule  $F_4TCNQ$ , we report the kinetic study on the direct interaction of Ag NPs with  $F_4TCNQ$  molecules in water-free organic solvent in this work. As shown in scheme 1, the surface of the Ag NPs has been firstly modified with dodecanethiol (DDT) to enable the phase-transfer from water to chloroform. Following the addition of  $F_4TCNQ$  molecules into the Ag NPs dispersed in chloroform solution, the ionization of  $F_4TCNQ$  is observed to occur first. Subsequently, the formation of Ag- $F_4TCNQ$  complex takes place, as manifested by UV-vis-NIR spectroscopy. The Ag- $F_4TCNQ$  solid has been further proved by cryogenic transmission electron microscopy (cryo-TEM) image, scanning nano-beam electron diffraction (NBED) and electron energy loss spectroscopy (EELS). Besides, a control experiment using silica-

coated Ag NPs reveals that a silica spacer of 18 nm has eliminated the whole effects, e.g. the charge transfer from Ag NPs to F<sub>4</sub>TCNQ and the formation of Ag-F<sub>4</sub>TCNQ complex.



Scheme 1: The schematic illustration of the interaction between the Ag NPs and  $F_4TCNQ$  molecules in the organic chloroform solution.

## **Results and discussion**

Silver nanoparticles (Ag NPs) have been synthesized by using sodium citrate to reduce silver nitrate in water/glycerol solution.<sup>31</sup> The as-synthesized Ag NPs with an average diameter of 28.0  $\pm$  3.4 nm are roughly spherical as can be seen from the TEM image in Figure 1a. The localized surface plasmon resonance (LSPR) of the Ag NPs in water centers at 400 nm as shown in Figure 1b, which is in good agreement with the previous report.<sup>31,32</sup> The as-prepared Ag NPs can be well dispersed in aqueous solution thanks to the hydrophilic citrate-stabilized surface, but aggregate in

organic solvents, such as acetonitrile and chloroform (see Figure S1 in Supporting Information). On the contrary, F4TCNQ generates radical anion easily and can be ionized progressively in polar solvent like water, but presents good stability and solubility in organic solvent like chloroform.<sup>33</sup>, <sup>34</sup> Therefore, a complete transfer of Ag NPs from water to chloroform is essential to facilitate the kinetic study, which eliminates the ionization of F<sub>4</sub>TCNQ caused by aqueous solution itself. Surface modification of Ag NPs is carried out as shown in Scheme 1: thiolated poly(ethylene glycol) (PEG-SH) and dodecanethiol (DDT) are used to modify the silver nanoparticles surface with a thin surfactant layer (surface coverage of PEG-SH on the Ag NP is at maximum 0.89 per nm<sup>2</sup>).<sup>35</sup> DDT serves as the hydrophobic capping agent and PEG-SH serves as the pre-stabilizer (See Method section for details). After the transferring of Ag NPs to chloroform, a red-shift of the LSPR band from 401.5 nm (in water) to 426.6 nm (in chloroform) has been observed as shown in Figure 1b, owing to the LSPR dependency on the surrounding medium, where the organic solvent possesses a higher refractive index.<sup>31, 32</sup> Complete phase transfer of Ag NPs from water to chloroform has been achieved as indicated by the photograph in Figure 1c: visually concomitant transfer of yellow color for silver nanoparticles from water (top phase) to chloroform (bottom phase). The TEM image of the Ag NPs shown in Figure 1d indicates that Ag NPs preserve their particle size and shape upon phase transfer process without aggregation, which is essential for the following study on the direct interaction between Ag NPs and F<sub>4</sub>TCNQ molecules.<sup>32, 35, 36</sup>



Figure 1. (a) TEM image of the as-synthesized silver nanoparticles which was dispersed in water before drying. (b) UV-vis-NIR absorption spectra of silver nanoparticles in water and after phase transfer in chloroform. (c) The photographs of the silver nanoparticles phase transferred from water to chloroform solution successfully after the ligand exchange. (d) TEM image of the surface modified-silver nanoparticles which was dispersed in chloroform before drying.

Chloroform is a good solvent for  $F_4TCNQ$ . As shown in the UV-vis-NIR absorption spectra of the  $F_4TCNQ$  molecules dissolved in chloroform (Figure 2a), two typical absorption peaks at 392.8 nm and 371.1 nm can be observed obviously, which are described by the intrinsic HOMO-LUMO electronic structure in quinoidal compounds. The two absorption peaks centered at 392.8 nm and

371.1 nm are assigned to the  $S_0$ - $S_1$  transition and the vibronic replication in neutral F<sub>4</sub>TCNQ molecules in chloroform, respectively.<sup>37-39</sup> The UV-vis-NIR absorption spectra of neutral F<sub>4</sub>TCNQ molecules suggests that no ionization occurs in chloroform. Before the study of the interaction between Ag NPs and F4TCNQ molecules in organic solution, we have carried out the blank experiments by mixing F4TCNQ molecules (chloroform solution) with PEG-SH (chloroform solution) or the cleaning solution, respectively. The UV-vis-NIR absorption spectra for blank experiments in Figure S2 and S3 show the same results as neutral F4TCNQ molecules which excludes the impurities influence from PEG-SH and cleaning solution. Afterwards, different amount of F4TCNQ molecules (0.6 µM to 30.0 µM) has been added into 3 ml chloroform solution with Ag NPs ( $c_{AgNPs} = 8.24 \times 10^{-10}$  M, which corresponds to the atomic concentration of Ag of 6.87  $\times 10^{-4}$  M). Figure 2b presents the UV-vis-NIR absorption spectra of the mixture solution recorded instantly after the addition of F<sub>4</sub>TCNQ. With the increase of the F<sub>4</sub>TCNQ molecules concentration from 0.6 µM to 30.0 µM, the absorption of Ag NPs at the grey area in Figure 2b shows a gradual red-shift, indicating the gathering of the adsorbed F4TCNQ molecules at the Ag NPs surface. In the meantime, new absorption peaks at 752.6 nm and 855.4 nm appear and the absorption intensities increase accordingly, indicating the ionization of F4TCNQ takes place.<sup>18, 34, 40</sup> It is attributed to the fact that the electron transfer from Ag NPs to F<sub>4</sub>TCNQ molecules occurs,<sup>30, 41</sup> which leads to positively charged Ag NPs and F4TCNQ<sup>-</sup> anions. As exemplified in the energylevel diagram of Ag NPs and F4TCNQ (inset of Figure 2c), the electron affinity of the F4TCNQ molecule is 4.93 eV and the work function of Ag NPs is 4.5 eV.<sup>42</sup> Therefore, the Femi energy level of Ag NPs is located higher than the lowest unoccupied molecular orbital (LUMO) of F4TCNQ, resulting to the direct injection of the electrons from Ag NPs to F<sub>4</sub>TCNQ upon adsorption.<sup>43</sup> The intensities of these anion absorption peaks increase gradually along with the molar ratio of

 $F_4TCNQ$  molecules to Ag NPs. When the concentration of  $F_4TCNQ$  molecules reaches 12.0  $\mu$ M, a new peak at 615.0 nm appears which is derived from the presence of Ag-F<sub>4</sub>TCNQ complex.<sup>14</sup>,  $^{30, 44, 45}$  It is known that the dimer of the F<sub>4</sub>TCNQ<sup>-</sup> performs the absorption peaks at both 620.0 nm and 886.0 nm. 44, 46-48 However, the low energy absorption of the dimer is absent in our measurements. Therefore, we assign the peak at 615.0 nm to the formation of Ag-F<sub>4</sub>TCNQ complex, rather than the dimer of  $F_4TCNQ^2$ . The appearance of the absorption peak at 615.0 nm is accompanied by the intensity decreasing of Ag NPs marked as gray area in Figure 2b, which is caused by the interaction between Ag NPs and F4TCNQ molecules to form Ag-F4TCNQ complex.<sup>29</sup> With the increasing of the concentration of F<sub>4</sub>TCNQ molecules, the absorption intensity of peak at 615 nm increases continuously and sharply, which can be observed clearly in Figure 2c. The intensity changes of absorption peaks at 855.4 nm (representing the F<sub>4</sub>TCNQ<sup>-</sup>) and 615.0 nm (representing the Ag-F<sub>4</sub>TCNQ) versus the molar ration of F<sub>4</sub>TCNQ: Ag NPs is shown in Figure S4. The absorption peak's intensity at 855.4 nm keeps constant after the molar ratio reaching  $1.464 \times 10^4$  due to the full coverage of F<sub>4</sub>TCNQ on the Ag NP ((5.18 F<sub>4</sub>TCNQ molecules per nm<sup>2</sup> of the Ag NP), while the absorption peak's intensity at 615.0 nm increases sharply. This could be attributed to the reason that more and more F4TCNQ<sup>-</sup> joined into the formation of Ag-F4TCNO complex. It has been also confirmed visually by the color change of the mixture solution in Figure 2d: the color of Ag NP solution in chloroform turns from yellow to blue-green after the concentration of F4TCNQ molecules reaches 30.0 µM. Further proof is gained from the cryo-TEM image shown in Figure 2e-f, which is a promising method to investigate the morphology of Ag-F4TCNQ complex in organic solution in situ. Compared to the well-dispersed pure silver nanoparticles in chloroform shown in Figure 2e, abundant packing structures surrounding the silver nanoparticles are clearly observed in Figure 2f after the addition of F4TCNQ molecules.



Figure 2. (a) UV-vis-NIR absorption spectra of different concentrations of pure F<sub>4</sub>TCNQ molecules from 0.6  $\mu$ M to 30.0  $\mu$ M in 3 ml chloroform. (b) UV-vis-NIR absorption spectra of silver nanoparticles in chloroform ( $c_{AgNPs}$ = 8.24 × 10<sup>-10</sup> M, which corresponds to the atomic concentration of Ag of 6.87 × 10<sup>-4</sup> M) recorded instantly after the addition of different amount of F<sub>4</sub>TCNQ (from 0.6  $\mu$ M to 30.0  $\mu$ M). (c) Zoom in the wavelength range from 550 nm to 1000 nm extracted from Figure 2b, the inset illuminates the energy-level diagram of the Ag NPs and F<sub>4</sub>TCNQ. (d) The photograph of Ag NPs in chloroform. (e) Cryo-TEM image of the pure silver nanoparticles which was dispersed in chloroform before freezing. (f) Cryo-TEM image of the mixture of Ag NPs with 30.0  $\mu$ M F<sub>4</sub>TCNQ solution.

The chemical composition investigation of the Ag-F<sub>4</sub>TCNQ complex has been carried out by electron energy loss spectroscopy (EELS). STEM-EELS results are shown in Figure 3. The high

angle annular dark field (HAADF) image is presented in Figure 3a for the mixture of F4TCNQ molecules with Ag NPs solution deposited on a thin carbon-coated copper grid. The dashed arrow depicted in Figure 3a indicates the analyzed EELS spectrum area, which covers an Ag NP (bright area labelled as 3) surrounded by F<sub>4</sub>TCNQ solid (grey area labelled as 2) and empty areas (dark areas labelled as 1 and 4). The carbon and silver energy loss are detected at 284 and 367 eV, respectively, as shown in selected spectra 1-4 in Figure 3b. Also shown in these panels, the silver signature is not only strongly detected on top of the Ag NP, but also weakly observed at the  $F_4TCNQ$  region, see spectra 2 and 3, respectively. Note that, given the shifted nature of the M<sub>4.5</sub> edge, although the edge threshold is observed at 367 eV, the maximum is measured at a considerably higher energy-loss. Such distribution of silver outside of the Ag NP is clearly revealed in the multivariate analysis of this EELS spectrum line, performed after background subtraction, as shown in Figure 3c and 3d. This analysis shows that the EELS signal can be expressed in terms of 3 contributions, which are as indicated by the color-coded labels corresponding to the Ag NP, F4TCNQ and grid materials, respectively. Region 2, corresponding to the F<sub>4</sub>TCNQ material, contains a mixture of the carbon and silver signatures, manifesting the presence of Ag and F<sub>4</sub>TCNQ in region 2. It leads us to the conclusion that the Ag-F<sub>4</sub>TCNQ complex forms at this region.



Figure 3. (a) HAADF image of the mixture of Ag NPs with  $30.0 \mu$ M F<sub>4</sub>TCNQ solution. An EELS spectrum line was acquired following the profile indicated with an arrow. (b) Four characteristic spectra selected from this line, their spatial origin indicated in the previous image using labels and color-coding, the spectra from region 1 and 4 are similar and overlapping here. (c, d) Multivariate analysis (non-negative matrix factorization decomposition algorithm) of the background subtracted EELS data showing three dominant components. For each component, an abundance profile in panel (c) shows its spatial distribution and a factor in panel (d) shows its characteristic spectral shape. A detailed discussion of these is given in the main text.

Scanning nano-beam electron diffraction (NBED) in the TEM has been used to investigate the crystallinity of the Ag NP and F4TCNQ system. Figure 4a shows that the beam raster covered a large region (~750 nm × 750 nm) containing a mixture prepared from Ag NPs with 30.0 µM F4TCNQ solution, which is deposited on an amorphous carbon grid. As is clearly shown in Figure 4a, the bright spots represent the agglomerate Ag NPs and the grey parts represent the surrounding F4TCNQ molecules on the carbon grid (black). The NBED patterns, see panels b to c, account for diffraction produced from small volumes, as the beam diameter is reduced close to 1.5 nm. This allows to distinguish regions, where the characteristic diffraction pattern of isolated Ag NPs is detected (see panels b-c), and other regions, where more complicated diffraction patterns are measured (d-e). The Ag NP patterns are compared to high-resolution TEM data, obtained from an isolated particle, see Figure 4f. The hexagonal patterns obtained from Fourier transform (FT) diffractogram analysis of this image,<sup>49</sup> see panels g-i, serve as the confirmation of the observed Ag NP NBED patterns 4b and 4c. We associate the more complicated patterns 4d and 4e with the diffraction of the formed Ag-F<sub>4</sub>TCNQ complex, which has been confirmed by the optical absorption and EELS analysis.



Figure 4. (a) Virtual dark-field image from scanning nano-beam diffraction (NBED) dataset covering a large region containing several Ag NPs (bright) and surrounding F<sub>4</sub>TCNQ material (grey) deposited on an amorphous carbon grid (dark). (b-e) Selected NBED patterns showing: (b,

c) the characteristic diffraction from Ag NP; (d, e) more complicated patterns associated with the presence of F4TCNQ material. The spatial origin of these four NBED patterns is indicated in (a) using labeled red squares. (f) High resolution TEM image of a single isolated Ag NP, with RGB coloring corresponding to the distribution of characteristic spatial motifs detected by Fourier transform (FT) diffractogram analysis. (g-i) The three FT diffractogram patterns corresponding to the Ag NPs, with (g) and (h) showing good correspondence to the NBED patterns in (c) and (d), respectively.

To gain in-depth insight into the interaction behavior between Ag NPs and F4TCNQ molecules, a time-dependence kinetic study employing UV-vis-NIR absorption spectra of Ag NPs ( $c_{AgNPs} = 8.24$  $\times 10^{-10}$  M) with different amount of F<sub>4</sub>TCNQ in chloroform solution has been performed. We have increased the F4TCNQ concentration from 3.6 µM to 30.0 µM, and recorded UV-vis-NIR absorption spectra in the time range from 0 seconds to 10 minutes with a time interval of several seconds, individually, as shown in Figure S5 for the full version. To improve the visualization of the curves, we plot the typical curves in Figure 5a-e with zoom part of the wavelength from 550 to 1000 nm. In Figure 5a, 3.6 µM F4TCNQ has been mixed with Ag NPs in chloroform. Once after the addition of the F4TCNQ molecules, the absorption intensity of Ag NPs at 426.6 nm decreases immediately and a red shift is observed over time. It is worth to mention that the typical absorption of F<sub>4</sub>TCNQ is blocked by the strong absorption of Ag NPs at the wavelength range from 300 to 450 nm as the concentration of F4TCNQ molecules is low. However, two absorption peaks related to F<sub>4</sub>TCNQ anions at 752.6 nm and 855.4 nm appear and their absorption intensities reach maximum spontaneously upon mixing, then decrease with time gradually. Similar phenomenon has been observed when the concentration of F4TCNQ is increased to 8.4 µM (Figure 5b). At this

concentration of  $F_4TCNQ$ , the typical  $F_4TCNQ$  absorption at 392.8 nm and 371.1 nm can be observed at the initial stage (0 - 10 s), then the intensities decrease gradually over time. In addition, an absorption peak at 416.5 nm appears, together with the peaks at 752.6 nm and 855.4 nm, due to the fact that F4TCNQ molecules are ionized to F4TCNQ<sup>-.50</sup> Increasing the F4TCNQ concentration to 12.0 µM, a new absorption peak at 615.0 nm arises and its intensity increases with time, while the typical absorption peaks of F<sub>4</sub>TCNQ ionization at 416.5 nm, 752.6 nm and 855.4 nm are still present and decreasing over the same time. To monitor the detailed kinetic process, we extract the intensity of the absorption peak of neutral  $F_4TCNQ$  molecules at 392.8 nm and the ionization peak of  $F_4TCNQ^2$  at 855.4 nm versus the adsorption time as shown in Figure S6. The absorption intensity of the neutral molecules is found to decrease from 0.38 to 0.29 in the period of 0 s to 60 s, demonstrating that the neutral F4TCNQ molecules are consumed after their adsorption on the surface of Ag NPs (Figure S6a). The consumption trend is also observed for the ionized molecules as shown by slight decreasing of the peak intensity of  $F_4TCNQ^2$  at 855.4 nm (Figure S6b). In addition, a new absorption peak at 615.0 nm arises and its intensity increases with time, which implies that the formation of Ag-F<sub>4</sub>TCNQ nanostructures.<sup>12, 14, 30</sup> Whereas in Figure 5a and b, the absorption of the initial formed Ag- $F_4$ TCNQ complex is too weak to be observed at 615.0 nm due to its low concentration, which is overlapped by the absorption of Ag NPs. The same phenomena could be observed when the concentration of  $F_4TCNQ$  increases to 18.0  $\mu$ M as shown in Figure 5d. Therefore, the typical kinetic process has been revealed in Figure 5f by tracking the change of absorption intensities at 855.4 nm (ionization of F<sub>4</sub>TCNQ) and 615.0 nm (formation of Ag- $F_4TCNQ$  complex) versus time, respectively. The absorption intensity at 855.4 nm decreases from 0.198 to 0.152 with time, while the one at 615.0 nm increases concomitantly from 0.061 to 0.083 and becomes constant in the end, clearly demonstrating that the self-assembling of AgF4TCNQ takes place followed the ionization of F4TCNQ. When the concentration of F4TCNQ reaches  $30.0 \mu$ M (Figure 5e), the absorption intensity of peaks at 615.0 nm, 855.4 nm and 752.6 nm remains constant with the time elapsing after mixing. This is due to the extremely fast interaction of F4TCNQ with Ag NPs at high concentration of F4TCNQ, which is out of the time resolution range of our experiment setup. It is worth noting that the intensity of the absorption peak of Ag NPs at 426.6 nm decreased from 0.523 to 0.096 and red-shifted over time as shown in Figure 5e. This can be ascribed to the adsorption of F4TCNQ molecules at the Ag NPs' surface and the formation of Ag-F4TCNQ complex surrounding the Ag NPs. Such formed Ag-F4TCNQ complex at the Ag NPs' surface leads to the slightly upward background at the high wavelength absorption in Figure 5c-e.

The ionization of F<sub>4</sub>TCNQ is instantaneous and the absorption intensity reaches the maximum in very initial time, as can be observed in all cases in Figure 5. The gradual decrease in the absorption intensity at 855.4 nm is due to the consumption of F<sub>4</sub>TCNQ<sup>-</sup> in the interaction with Ag NPs to form the Ag-F<sub>4</sub>TCNQ complex. Considering that the atomic concentration of Ag ( $c_{Ag}$ = 6.87 × 10<sup>-</sup> <sup>4</sup> M) is much more excess than that of the F<sub>4</sub>TCNQ molecules ( $c_{F4TCNQ}$  = 12.0 µM), the interaction here is described as the first order reaction: Ag + F<sub>4</sub>TCNQ  $\rightarrow$  Ag-F<sub>4</sub>TCNQ.<sup>29, 51</sup> It is known that the first-order reaction rate is proportional to the reactant concentration in the system, <sup>52</sup> Therefore, we track the kinetics of the interaction under a slow reaction rate via decreasing the reactant concentration. The first-order process rate is accordingly calculated by extracting the absorption intensity change at 855.4 nm to further study the kinetic mechanism. The relationship of  $-\ln(A/A_0)$  versus time is employed, in which A is the absorption intensity at 855.4 nm at each time interval while A<sub>0</sub> is the instant absorption intensity at 0 s in Figure S7. With the increasing of F<sub>4</sub>TCNQ molecules concentration from 8.4 µM to 12.0 µM, the rate decreases from 0.157 min<sup>-1</sup> to 0.109

min<sup>-1</sup> ascribing to the overlapped coverage of  $F_4TCNQ$  molecules on Ag NPs, which slows down the interaction between  $F_4TCNQ$  molecules and Ag NPs. However, the formation of Ag- $F_4TCNQ$ complex is boosted after the addition of  $F_4TCNQ$  of 12.0 µM with a molar ratio to Ag NPs at 1.464 ×10<sup>4</sup> (5.18  $F_4TCNQ$  molecules per nm<sup>2</sup> of the Ag NP) as discussed before, manifested by the sharply increased absorption intensity at 615.0 nm. With the successive increasing of the  $F_4TCNQ$ molecules concentration to 18.0 µM, the rate continues decreasing to 0.064 min<sup>-1</sup>. It is supposed to be caused by the formation of Ag- $F_4TCNQ$  complex surrounding the Ag NPs in a large scale, which further hinders the interaction of Ag NPs and  $F_4TCNQ$ . The result is well supported by the breakneck increasing of the Ag- $F_4TCNQ$  complex absorption intensity at 615.0 nm when the concentration of  $F_4TCNQ$  reaches 12.0 µM. Hence, from the kinetic analysis, the concentration of  $F_4TCNQ$  molecules plays a crucial role for triggering the formation of Ag- $F_4TCNQ$  complex in a large amount.



Figure 5. Kinetic study of UV-vis-NIR absorption spectra of silver nanoparticles in chloroform  $(c_{AgNPs}=8.24 \times 10^{-10} \text{ M}, \text{ which corresponds to the atomic concentration of Ag of 6.87 \times 10^{-4} \text{ M})$  with different concentration of F<sub>4</sub>TCNQ: (a) 3.6 µM, (b) 8.4 µM, (c) 12.0 µM, (d) 18.0 µM, (e) 30.0 µM. (f) Characteristic peaks at 615.0 nm and 855.4 nm extracted from UV-vis-NIR spectra to monitor the interaction between Ag NPs and 18.0 µM F<sub>4</sub>TCNQ at different time.

On the basis of these observations, we propose the schematic process of  $F_4TCNQ$  molecules on the surface of Ag NPs in chloroform. It involves two steps: firstly, the instantaneously adsorbed  $F_4TCNQ$  molecules on the Ag NPs surface induce the electron transfer from Ag NPs to  $F_4TCNQ$ molecules and endow the silver nanoparticles surface positive charges.<sup>30, 41</sup> Simultaneously and correspondingly, the ionization from  $F_4TCNQ$  to  $F_4TCNQ^-$  takes place in succession. Afterwards, the formation of Ag-F<sub>4</sub>TCNQ complex is driven with the Ag<sup>+</sup> ions.

To further study the surface interaction between silver nanoparticles and F<sub>4</sub>TCNQ molecules, the silica-coated silver nanoparticles (SiO<sub>2</sub>@Ag NPs) have been fabricated followed the modified Stöber method.<sup>53-55</sup> As can be seen in the inset of Figure 6a, the silica-coated silver nanoparticles have been achieved with an average silica shell thickness of  $(17.8 \pm 2.0)$  nm. Similarly, surface modification on silica shell with amino groups using (3-aminopropyl)triethoxysilane (APTES) dehydration has been performed to transfer the silica-coated Ag NPs from ethanol to chloroform.<sup>56</sup> UV-vis-NIR absorption spectra of the silica-coated silver nanoparticles in ethanol and chloroform show similar characteristic peak at 414.0 nm in Figure 6a without shape change and peak broadening, indicating the complete phase transfer from ethanol to chloroform for silica-coated silver nanoparticles.



Figure 6. (a) UV-vis-NIR absorption spectra of SiO<sub>2</sub>@Ag NPs in ethanol and chloroform. The inset shows the TEM image of SiO<sub>2</sub>@Ag NPs in ethanol. (b) UV-vis-NIR absorption spectra of SiO<sub>2</sub>@Ag NPs in chloroform with different amount of F<sub>4</sub>TCNQ, the inset shows the photograph SiO<sub>2</sub>@Ag NPs in chloroform before and after the addition of the F<sub>4</sub>TCNQ molecules.

The interaction between F<sub>4</sub>TCNQ molecules and the silica-coated Ag NPs has been investigated following the same procedure of the pure Ag NPs. In Figure 6b, different amount of F<sub>4</sub>TCNQ molecules from  $3.6 \,\mu$ M,  $8.4 \,\mu$ M,  $18.0 \,\mu$ M,  $24.0 \,\mu$ M to  $36.0 \,\mu$ M have been added into the SiO<sub>2</sub>@Ag NPs( $c_{SiO2@AgNPs} = 7.2 \times 10^{-10}$  M) dispersed in chloroform solution. Characteristic peaks of F<sub>4</sub>TCNQ molecules at 371.1 nm and 392.8 nm are found. With the increase of the F<sub>4</sub>TCNQ amount, the absorption intensities of these two peaks improve. However, no additional peaks appear during the whole process, indicating no ionization of F<sub>4</sub>TCNQ occurs in this case. This confirms that the charge transfer from Ag NPs to F<sub>4</sub>TCNQ molecules, ionization of F<sub>4</sub>TCNQ molecules and the formation of Ag-F<sub>4</sub>TCNQ complex have been prohibited by the silica shell.

### Conclusion

In summary, we reported the full kinetics study on the self-assembling of  $F_4TCNQ$  molecules directly on the surface of Ag NPs in chloroform solution. The surface modification of Ag NPs with PEG-SH and DDT enables the phase transfer of Ag NPs from water to chloroform. By following the UV-vis-NIR absorption spectra of the mixture of  $F_4TCNQ$  molecules and Ag NPs in chloroform solution, a two-step process has been discovered, which consists of the electron transfer from Ag NPs to  $F_4TCNQ$  and the ionization of  $F_4TCNQ$ , followed by the formation of Ag- $F_4TCNQ$  complex with the synergy of Ag<sup>+</sup> ions. The formation of Ag- $F_4TCNQ$  solid has been further confirmed by cryo-TEM, NBED and EELS results. The kinetic study has gained insight into the interaction mechanism between Ag NPs and  $F_4TCNQ$  organic molecules, which offers new options and guidance to the further control in the unique electronic and photoactive properties of the charge transfer complex for the application in organic electronic devices.

#### **Method Section**

**Materials**. Silver nitrate (99%), sodium citrate (Na3Cit), glycerol, tetraethyl orthosilicate (TEOS), (3-aminopropyl)triethoxysilane (APTES), chloroform (Anhydrous) (99.4%), chloride acid (37%), ammonia solution (28 wt%), 2,3,5,6-tetrafluor-7,7,8,8-tetracyan-chinodimethan (F<sub>4</sub>TCNQ), thiolated poly(ethylene glycol) (PEG-SH, MW 5000 g mol<sup>-1</sup>), dodecanethiol (DDT) and absolute ethanol were purchased from Aldrich. All the chemicals were used without further purification.

**Synthesis of silver nanoparticles.** Spherical silver nanoparticles have been synthesized following a modified protocol of Steinigeweg and Schlücker.<sup>31</sup> In a typical run, 50 ml water/glycerol (40 v/v % glycerol) mixture has been heated to 95 °C. To this solution, 9 mg AgNO<sub>3</sub> was added and stirred

at 500 rpm for 1 min. 30 mg Na<sub>3</sub>Cit was added as reducing agent and the mixed solution was then stirred for 1 h at 500 rpm at 95 °C. The mixture turned from yellow to orange after 10 min and became turbid. After 1 h the solution was strongly turbid and appeared to be yellow-green. After the reaction cooled down to room temperature, silver nanoparticles were collected after 3 times centrifugation and washing with water then stored at 4 °C in 50 ml water. The solution was calibrated by solid content weight to give the  $c_{Ag}=7.5 \times 10^{-4}$  M.

**Phase transfer of silver nanoparticles.** As-prepared silver nanoparticles were transferred from water to chloroform. 10 ml of above aqueous silver nanoparticle dispersion was first stabilized with 0.12 mg PEG-SH. Subsequently, a 10 ml of DDT solution in CHCl<sub>3</sub> (10 µl/ml) was added to the aqueous phase containing the Ag NPs. Phase transfer occurred after vigorous stirring for periods of 15 min. The transfer was assisted by addition of 20 µL of concentrated HCl (37%). Silver nanoparticles were then collected by centrifugation and stored at 4 °C in choroform.<sup>35</sup> The atomic concentration of Ag is calculated by the solid content weight of silver, which leads to  $c_{Ag}$ = 6.87 × 10<sup>-4</sup> M. The nanoparticles concentration of Ag nanoparticles is calculated by the solid content weight base on the single silver nanoparticles with the radius of 15 nm to give the  $c_{AgNPs}$ = 8.24 × 10<sup>-10</sup> M (Details see in the Supporting Information).

**Silica coating of silver nanoparticles.** For the silica coating, 10 ml of the as-synthesized Ag NPs solution was mixed with 30 µl TEOS to achieve the mixed solution. In the meantime, 1 ml ammonia solution was added into 30 ml ethanol with continuous stirring to achieve the mixture solution. After 1 h, the mixture of ammonia in ethanol solution was added into the mixture solution of Ag NPs with TEOS dropwise. After stirring at room temperature for 15 minutes, the silica-

coated silver nanoparticles were collected by centrifugation and washed by ethanol for several times, and then stored at 4 °C for further phase transfer into chloroform.

**Phase transfer of silica-coated silver nanoparticles.** Briefly, a certain concentration of APTESethanol-water (1:5:1 by volume) solution was prepared for hydrolyzing 3h before use. 200 µl the above hydrolyzing solution was added dropwise to the 10 ml above silica-coated silver nanoparticles solution under stirring at 60 °C for 12 h with refluxing. Then modified silica-coated silver nanoparticles were collected by centrifugation and re-dispersed in the chloroform.

**Transmission electron microscopy.** The morphology of the nanoparticles was investigated by transmission electron microscopy (TEM) using a JEOL JEM-2100 (JEOL GmbH, Eching, Germany) at an acceleration voltage of 200 kV. Samples were prepared by placing a drop of the diluted nanoparticles solution on the carbon-coated copper grids and dried under ambient temperature.

**Ultraviolet-visible-near infrared absorption spectroscopy.** The ultraviolet-visible-near infrared absorption spectra (UV-vis-NIR absorption spectra) were measured by Agilent 8453. In a typical run of the kinetic study on the interaction between  $F_4TCNQ$  molecules and Ag NPs, 3 ml of Ag NPs ( $c_{Ag}$ = 6.87 × 10<sup>-4</sup> M) was added in a cuvette, then a certain amount of the F4TCNQ molecules solution in chloroform was supplemented. The spectra were immediately recorded by the UV-vis-NIR absorption spectroscopy and a series of rounds were collected in a time interval of several seconds. For the statistical analysis, all the measurements have been repeated for three times under

the same condition. All the measurements were conducted under the same operating conditions including a constant temperature of 20  $^{\circ}$ C.

**Cryogenic transmission electron microscopy.** Cryo-TEM specimens were vitrified by plunging the samples into liquid ethane using an automated plunge freezer (Vitrobot Mark IV, FEI). The lacey carbon copper grids (Science Services) were pretreated by 10 seconds of glowing discharge and equilibrated for 5 minutes. After blotting the liquid, the specimens were vitrified and inserted into a pre-cooled Gatan 914 sample holder and transferred into a JEOL JEM-2100, operating at 200 kV.

**Electron energy-loss spectroscopy**. STEM-EELS experiments were performed in a JEOL 2200 equipped with field-emission gun and omega filter. A beam shower procedure was employed to reduce beam-induced contamination. Multidimensional analysis was used to process spectrum images datasets, employing the non-negative matrix factorization (NMF) algorithm to unravel the signals in the C-K and Ag- $M_{4,5}$  range (~ 300 eV).

Scanning nano-beam electron diffraction. Scanning NBED datasets were acquired also in the above mentioned JEOL 2200 TEM. Aiming for a small beam size of ~ 1.5 nm ensured that the obtained diffraction patterns contained scattering from small volumes of the sample. These data are compared to characteristic isolated Ag NP patterns obtained by Fourier transform (FT) diffractogram analysis of high-resolution TEM, using home developed software.<sup>49</sup>

#### **Supporting Information**

The Supporting Information is available and free of charge for:

The caculation of the concentration of Ag NPs; Photos of Ag nanoparticles redispersed in chloroform and acetonitrile solvent without phase transfer modification; UV-vis-NIR absorption spectra of blank experiment for washing solvent with F<sub>4</sub>TCNQ in chloroform, bare PEG-SH, bare F<sub>4</sub>TCNQ in chloroform and the mixture of PEG-SH and F<sub>4</sub>TCNQ in chloroform; Characteristic peaks at 615.0 nm and 855.4 nm extracted from UV-vis-NIR absorption spectra; Full version kinetic study of UV-vis-NIR absorption spectra of silver nanoparticles in chloroform with F<sub>4</sub>TCNQ molecules; Characteristic peaks at 392.8 nm and 855.4 nm extracted from the UV-vis-NIR absorption spectra in Figure 5c to monitor the kinetic interaction between Ag NPs and 12.0  $\mu$ M F<sub>4</sub>TCNQ at different time; The plots of  $-\ln(A/A_0)$  versus time, in which A is the absorption intensity at 855.4 nm at each time interval while A<sub>0</sub> is the instant absorption intensity at 0 s for the different concentration of F<sub>4</sub>TCNQ mixed with Ag NPs.

#### Acknowledgement

Y. H. Zhao, Z. Kochovski and Y. Lu acknowledge the funding support of the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project number 182087777 - SFB 951 within project B2, A. Opitz and N. Koch acknowledge the funding support from SFB 951 within project A8, A. Eljarrat and C. T. Koch acknowledge the funding support from SFB 951 within project A12.

#### **Competing interests**

The authors declare no competing interests.

## Data availability statement

All data generated or analyzed during this study are included in this published article (and its

Supplementary Information files).

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The distinct kinetics and the influence of the molar ratio of Ag NPs/F<sub>4</sub>TCNQ molecules on the interaction between Ag NPs and F<sub>4</sub>TCNQ molecules in the organic solution are reported herein for the first time. It includes the first step of electron transfer from Ag NPs to F<sub>4</sub>TCNQ indicated by the instantaneous ionization of F<sub>4</sub>TCNQ, and the second step of the long-term formation of Ag- $F_4$ TCNQ complex.

Yuhang Zhao, Andreas Opitz, Alberto Eljarrat, Zdravko Kochovski, Christoph T. Koch, Norbert Koch and Yan Lu\*

Kinetic Study on the Adsorption of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane on Ag Nanoparticles in Chloroform: Implications for the Charge Transfer Complex of Ag-F<sub>4</sub>TCNQ

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